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Synthesis and characterization of boron nitride nanotubes using a simple chemical method

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A simple two-step process is used for the growth of high purity multiwalled boron nitride (BN) nanotubes. In the first step, disordered nanostructured BN powder (aBN) is prepared chemically by heating a powdered mixture of KBH_4 and NH_4Cl (1:1) at 850ºC in N_2 followed by quenching the reaction product. In the second step, BN nanotubes are grown from the as-prepared aBN powder by annealing it at about 1200-1300ºC for 5-10 h in N_2. No catalyst material (Fe, Ni, Co, etc.) is intentionally added to aBN powder. This method of synthesis resulted in high purity multiwalled BN nanotubes of almost uniform diameter (10-30 nm) and length up to 5 µm, and, thus has a high aspect ratio with inherent characteristics of BN nanotubes, which may be useful for different applications. The BN nanotubes have been characterized using various techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The results obtained by this process are also compared with the similar type of BN nanotubes produced employing ball-milling and annealing technique.

After the discovery of carbon nanotubes (CNTs) in 1991, significant efforts have been made to synthesize BN nanotubes not only because of their similar nanostructures as possessed by carbon nanotubes but also because of many properties which are found to be superior to those of CNTs. Therefore, these BN nanotubes finds application in various electronic and mechanical devices[1]. With a wide band gap of about 5.5 eV, BN nanotubes have high resistance of oxidation and Young's modulus almost similar to that observed for carbon nanotubes (1 TPa) [2,3]. Carbon nanotubes have weak resistance to oxidation mainly due to their large surface area and defects at tips and these nanotubes readily oxidize in air at 400˚C and burn completely at 700˚C in oxygen atmosphere[4,5]. BN nanotubes are, however, found to be more stable up to about 1000˚C[6,7]. All these factors make BN nanotubes particularly useful for many nano technological applications where thermal stability, high strength and stable electrical performance are the major considerations.

Chopra *et al*.[2] have reported the synthesis of BN nanotubes for the first time using an arc discharge between tungsten electrodes filled with BN powder. Subsequently various techniques, such as, plasma arc-discharge[2,8], laser ablation[9], substitution reaction[10-12], ball milling-annealing[13-17] and chemical reactions[18-24] have been used for producing BN nanotubes. These methods are also employed for the synthesis of carbon nanotubes. Large quantities of BN nanotube can be synthesized employing ball milling followed by annealing process. This process is known as mechanothermal process. In this process nanostructured disordered BN or aBN powder is first prepared by ball milling elemental boron (B) or hexagonal boron nitride (hBN) powder for about 100-150 h in an inert atmosphere. BN nanotubes are grown by annealing the as-milled BN powder at 1000-1300ºC for 5-10 h in nitrogen containing atmosphere. However, the BN nanotubes produced using this process are generally contaminated with metals (Fe, Ni, Cr and W) coming from the abrasion of balls and containers during the ball milling[15,16] and, therefore, have to be subsequently purified.

Several chemical methods based on vapor-liquid-solid (VLS) mechanism[18,19] have been suggested for the formation of BN nanotubes. These methods involve a chemical reaction between elemental boron with transition metal oxides especially Fe_2O_3 or a mixture of boron, MgO and FeO powders. BN nanotubes were found to have formed within a wide temperature range of 1100-1700ºC in the presence of nitrogen or ammonia gas[19-24]. It has also been reported that carbon nanotubes could also be used as precursor along with MoO_3 as catalyst to synthesize BN nanotubes in the presence of B_2O_3 and N_2[12]. The key

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feature of these processes is the chemical reaction of NH_3/N_2 gas with B_2O_2 generated during the chemical reactions and thus producing BN nanotubes. In all these chemical reactions transition metals are believed to act as catalysts for the growth of BN nanotubes. Zhi *et al.*[23] have reported the synthesis of about 200 mg of highly pure BN nanotubes, having a diameter of about 50 nm by heating a mixture of FeO, MgO and B powder at 1500ºC in the presence of ammonia for about 1 h.

In the present work, we have used a simple technique of synthesizing disordered BN nanostructured powder employing a chemical route where the processing has been done in a much shorter duration. In this process, heating a mixture of KBH_4 and NH_4Cl in an inert atmosphere followed by quenching the reaction product has produced these BN nanostructures. These BN nanostructured powders were subsequently annealed at high temperatures in N_2 atmosphere to produce BN nanotubes. The main advantage of adopting this chemical method is that a much shorter duration is required to produce nanostructured BN powder as compared to that required in ball milling process. The other advantage is that BN nanotubes produced employing chemical method results in better purity.

Experimental Procedure

In the present investigations a mixture of KBH_4 and NH_4Cl (99.9 %, Merck, Germany) having a weight ratio of 1:1, was heated in a tubular furnace at temperatures ranging from 800 to 1000ºC in the presence of nitrogen atmosphere for about 2 h followed by quenching the reaction product in air. From a series of experiments, it was concluded that best results were obtained when this mixture was heated at about 850˚C.

The following chemical reaction took place in the preparation of nanostructured BN powder:

$$KBH_4 + NH_4Cl \xrightarrow{800\text{-}1000ºC,\ N_2} KCl + aBN + 4H_2$$

The degree of amorphosity of the product was found to depend on the rate of quenching. Fast quenching favored the formation of amorphous boron nitride (aBN) while slow quenching favored the formation of turbostratic boron nitride (a randomly oriented layered BN structure). In the present case the boat containing the reaction product was shifted from the center to the end of alumina tube where direct nitrogen supply was available to achieve a high quenching rate.

The disordered BN powder produced using the above mentioned chemical route was subsequently annealed in the temperature range of 1000-1300ºC for a duration of 5-10 h in the presence of nitrogen. This process of annealing converted the disordered BN powder into BN nanotubes.

BN nanotubes synthesized employing the present route of chemical reaction followed by annealing (as reported above) were compared with our earlier experiments where BN nanotubes were synthesized employing high-energy ball milling followed by annealing. In case of high-energy ball milling, hexagonal boron nitride (hBN) powder was first converted into nanosized amorphous BN powder using ball milling and this ball milled aBN powder was subsequently annealed to convert it into BN nanotubes[25]. It may be noted that the two separate methods namely the chemical route and the high energy ball milling were used only to synthesize disordered or aBN powder but in both the cases BN nanopowders were converted into BN nanotubes using the same process of annealing in a protective atmosphere. The ball milling experiments were carried out using a high-energy planetary ball mill (at a speed of about 300 rpm) where WC containers and balls were used to mill the hBN powder using liquid NH_3 solution as the milling medium. The balls to powder weight ratio was about 30:1. The as-milled powdered samples were also characterized by XRD after an interval of 40 and 100 h to observe the degree of amorphisation in BN samples.

The BN nanotubes produced using the two routes as stated above, i.e., chemical route followed by annealing and powder metallurgy (PM) route followed by annealing were compared employing XRD and TEM studies and the results of these characterizations are discussed.

Material characterization

BN nanotubes were dispersed on carbon coated copper grid of about 3 mm diameter having 200 mesh pore size, by making a suspension in acetone. Microstructural characterization at high magnifications and reciprocal space analysis were carried out using a transmission electron microscope (TEM, model JEOL JEM 200CX), operated at the electron accelerating voltage of 200 kV. A scanning electron microscope (SEM, model LEO 440) equipped with an energy depressive spectrometer (EDS, model Oxford Link ISIS 300) was used to study the topological features and the composition of

B and N at different regions of the powder material. Further crystallographic interpretations on the formation of different phases during synthesis of BN nanotubes was performed by X-ray diffraction (XRD) patterns recorded using a D8 Advanced Bruker Diffractometer.

Results and Discussion

X-ray characterization

Figure 1a shows an XRD pattern of aBN powder prepared chemically from KBH_4 and NH_4Cl. From this pattern, it is clear that the material is almost amorphous in nature. Surface microstructure of as prepared disordered BN powder exhibited that most of its particles were in the size range of 150-200 nm. This nanosized aBN powder was used for the growth of BN nanotubes during subsequent annealing. Figure 1b shows an XRD pattern of BN nanotubes produced from nanosized aBN powder by isothermal annealing at about 1200ºC for 10 h in nitrogen atmosphere. From this XRD pattern, it is clear that only well defined peaks of highly crystalline BN were observed and no other phases were present. Isothermal annealing transforms the highly disordered amorphous structure into a highly crystalline hexagonal BN structure (a = 0.251 nm, c = 0.669 nm). It may be mentioned that although one can obtain a large quantity of BN nanotubes by ball milling and annealing of B or hBN powders, as observed by earlier workers[13,16] the BN nanotubes were mostly contaminated with metallic inclusions due to the abrasion of metals from the walls of container during ball milling operation. However, using this two-step process employing chemical route followed by annealing for the synthesis of BN nanotubes, the purity level was relatively higher.

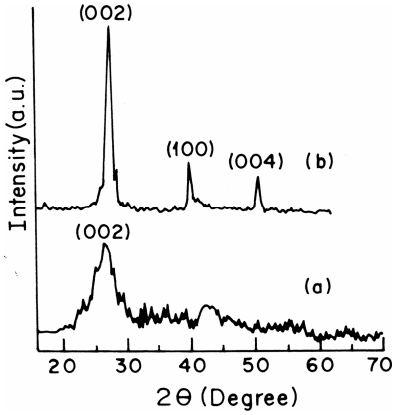

Fig. 1—XRD patterns of (a) amorphous BN powder and (b) BN nanotubes produced from aBN powder after annealing at 1200ºC in N_2 atmosphere

Figure 2a shows an XRD pattern of BN nanotubes produced using mechanothermal process where hBN powder was ball milled for 100 h and annealed at 1300ºC for 10 h in nitrogen atmosphere. From this XRD pattern, it is clear that product is contaminated with W impurities. At lower annealing temperatures (~ 950ºC), other phases, such as, W_2B_5 was also observed in the XRD pattern as shown in Fig. 2b. In the present method using a chemical route although the purity of BN nanotubes is relatively higher, the

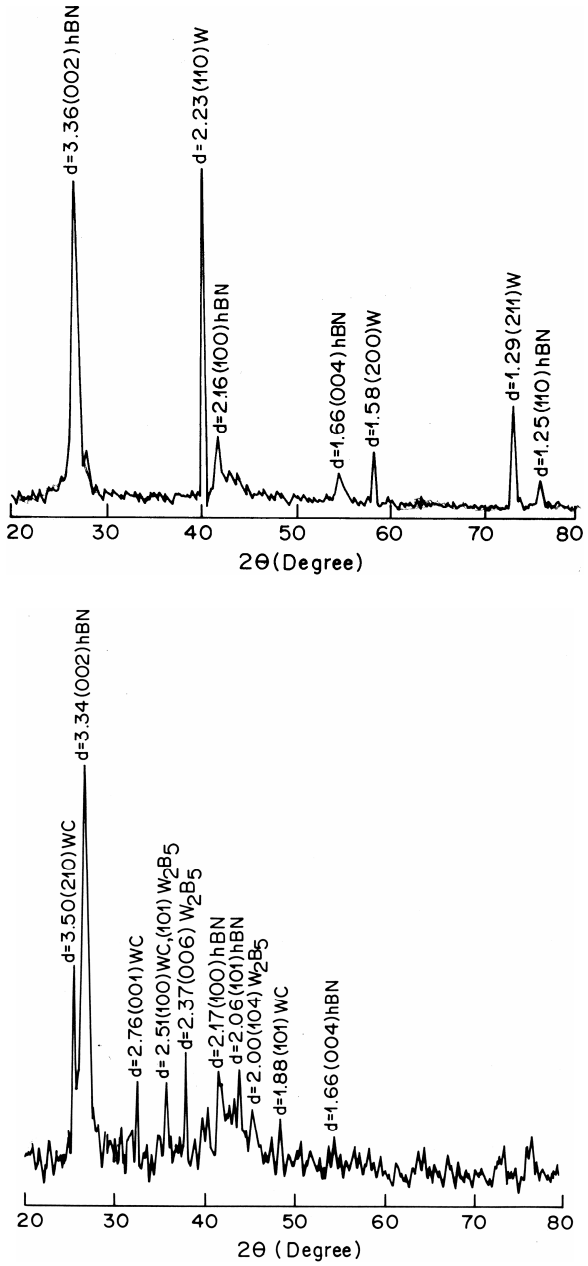

Fig. 2—XRD pattern of BN nanotubes produced from 100 h ball milled BN powder and annealing at (a) 1300°C and (b) at 950°C in N_2 atmosphere (*d* values in Å]